PATENT ABSTRACTS OF JAPAN

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(54) COATED MEMBER OF CERAMIC

(57)Abstract:
PURPOSE: To obtain a coated member of ceramics having excellent peel resistance of substrate from coated layer, improved heat resistance, thermal shock resistance and corrosion resistance.
CONSTITUTION: A coated layer is formed on the surface of a ceramic substrate of silicon nitride and the coated layer has a ground layer of an oxide having the same coefficient of thermal expansion as that of the substrate or close to that, an intermediate layer of an oxide formed on the surface of the ground layer and a surface layer of an oxide formed on the surface of the intermediate layer. The coated layer has an inclined structure of coefficient of thermal expansion sloping and gradually rising in the order of the ground layer, the middle layer and the surface layer. The ceramic substrate is selected from silicon nitride composite materials reinforced with dispersed silicon nitride and silicon carbide. The oxides are two or more selected from zircon, zirconia, alumina, mullite and yttria.

CLAIMS

[Claim(s)]
[Claim 1] The ceramic-coating member characterized by having the substrate layer of the oxide which has the coefficient of thermal expansion, the EQC, or the near coefficient of thermal expansion of a base material on the front face of a silicon nitride radical ceramic base material, the interlayer of the oxide formed in the front face of this substrate layer, and the surface layer of the oxide formed on this interlayer's front face, and having the inclination structure which a coefficient of thermal expansion inclines in order of said substrate layer, an interlayer, and a surface layer, and becomes high gradually.
[Claim 2] Said oxide is a ceramic-coating member according to claim 1 which is two or more sorts chosen from zircon, a zirconia, an alumina, a mullite, and yttria.

[Claim 3] Said interlayer is a ceramic-coating member according to claim 1 characterized by consisting of multilayer inclination structure which a coefficient of thermal expansion inclines and becomes high gradually as consist of a mixolimnion of said substrate layer and said surface layer, the mixed rate is made to incline gradually and it goes to said surface layer from said substrate layer.
[Claim 4] Said oxide is a ceramic member according to claim 1 characterized by thin film formation being carried out by the plasma metal spray on the front face of a silicon nitride radical ceramic base material.
[Claim 5] The manufacture approach of the ceramic-coating member characterized by covering the oxide which a coefficient of thermal expansion inclines one by one on the front face of the oxide, and becomes high gradually on it after covering the oxide which has the coefficient of thermal expansion, the EQC, or the near coefficient of thermal expansion of a base material on the front face of said silicon nitride radical ceramic base material.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the ceramic-coating member excellent in thermal resistance, thermal shock resistance, and corrosion resistance.
[0002]
[Description of the Prior Art] Conventionally, as an elevated-temperature structural material used by the severe condition at an elevated temperature, ceramic ingredients, such as silicon nitride and silicon carbide, are known. The silicon nitride sintering member with the zirconia enveloping layer shown in JP,62-72582,A as a heat-resistant good ceramic ingredient is known.
[0003]
[Problem(s) to be Solved by the Invention] However, also although such silicon nitride or silicon carbide is called elevated-temperature heat-resisting material, if it is exposed to the combustion gas in which these ingredients have the high-speed rate of flow, high temperature oxidation, high temperature corrosion, etc. will thin down a member in many cases. For this reason, in order to improve endurance about the member exposed to combustion gas with the high-speed rate of flow, it is an important technical problem to raise oxidation resistance.
[0004] Only by carrying out surface coating of the oxide ceramics on the surface of a base material according to the surface coating approach of such conventional oxide ceramics, although the approach of carrying out surface coating of the oxide ceramics for this technical-problem solution is proposed, if long duration use is carried out at an elevated temperature, it will originate in the difference between the coefficient of thermal expansion of a base material, and the coefficient of thermal expansion of oxide ceramics, stress distortion will become excessive by the boundary layer, and an enveloping layer will tend to exfoliate from a base material.
[0005] The purpose of this invention has the good peeling resistance of a base material and an enveloping layer, and it is to offer the ceramic-coating member excellent in thermal resistance, thermal shock resistance, and corrosion resistance, and its manufacture approach.
[0006]
[Means for Solving the Problem] The ceramic-coating member by this invention for

attaining said purpose The substrate layer of the oxide which has the coefficient of thermal expansion, the EQC, or the near coefficient of thermal expansion of a base material on the front face of a silicon nitride radical ceramic base material, It is characterized by having the interlayer of the oxide formed in the front face of this substrate layer, and the surface layer of the oxide formed in this interlayer's front face, and having the inclination structure which a coefficient of thermal expansion inclines in order of said substrate layer, an interlayer, and a surface layer, and becomes high gradually.

[0007] Said oxide is two or more sorts chosen from zircon, a zirconia, an alumina, a mullite, and yttria. Said interlayer consists of a mixolimnion of said substrate layer and said surface layer, and he consists of multilayer inclination structure which a coefficient of thermal expansion inclines and becomes high gradually as he makes the mixed rate incline gradually and goes to said surface layer from said substrate layer.

[0008] Thin film formation of said oxide is carried out by the plasma metal spray on the front face of a ceramic base material. The manufacture approach of said ceramic-coating member covers the oxide which a coefficient of thermal expansion inclines one by one on the front face of the oxide, and becomes high gradually on it, after covering the oxide which has the coefficient of thermal expansion, the EQC, or the near coefficient of thermal expansion of a base material on the front face of a silicon nitride radical ceramic base material.

[0009] Said substrate layer is precise, a layer with good adhesion with a base material and said interlayer have a micro crack, pore, etc., a porosity layer and said surface layer are precise, and the layer which has thermal resistance is desirable. 5-15 micrometers of thickness of a hit are 10 micrometers much more preferably. The whole enveloping layer thickness is 50-150 micrometers, and is 70-120 micrometers preferably. It is because an enveloping layer will tend to exfoliate if possibility of being unable to absorb thermal expansion as total enveloping layer thickness is less than 50 micrometers, and being divided is large and total enveloping layer thickness exceeds 150 micrometers.

[0010]

[Function] Since according to the ceramic-coating member of this invention the device in which the stress distortion between each class etc. is absorbed is generated in order that the value of a coefficient of thermal expansion may consider as the inclination enveloping layer structure which increases gradually as the typical sectional view of an enveloping layer is shown in drawing 1 and it goes to an interlayer 4 and a surface layer 5 from the substrate layer 3 of the enveloping layers 2 formed in the front face of the silicon nitride radical ceramic base material 1, the maximum stress at the time of stress generating is reduced. The ceramic member which has a coating layer with high resistance, such as a thermal shock, by this is obtained.

[0011] According to this ceramic-coating member, thermal shock nature improves by the inclination of the coefficient of thermal expansion of a surface coating layer, the oxidizing quality in an elevated temperature and corrosive are improved sharply, and a reliable ceramic-coating member is obtained.

[0012]

[Example] A substrate layer and the middle class were formed for the front face of a ceramic base material with 3mm [in test piece dimension width of face of 4mm, and thickness], and a die length of 50mm after surface roughening, and the surface layer of an alumina, a zirconia, or yttria was formed in the maximum surface by thermal spraying.

(1) Example The silicon nitride composite which carried out dispersion strengthening of silicon nitride or a silicon carbide particle, the whisker, etc. was used for 1 - 10 ceramic base material, and the enveloping layer used various oxides. An enveloping layer consists of a substrate layer, an interlayer, and a surface layer. The base material of each examples 1-10, a substrate layer, an interlayer, and a surface layer are as being shown in Table 1.

[0013]

[Table 1]

区分	セラミック基材	下地層の材料	中間層の材料	表面層の材料	剥離までの熱サイクル数	被膜層に亀裂が発生したアニール時間
実施例 1	窒化珪素	ジルコン	ジルコン／ジルコニア	ジルコニア	50回以上	150Hr 以上
実施例 2	窒化珪素	ジルコン	ジルコン／アルミナ	アルミナ	50回以上	150Hr 以上
実施例 3	窒化珪素	ジルコン	ジルコン／イットリア	イットリア	50回以上	150Hr 以上
実施例 4	窒化珪素	ムライト	ムライト／アルミナ	アルミナ	50回以上	150Hr 以上
実施例 5	窒化珪素	ムライト	ムライト／イットリア	イットリア	50回以上	150Hr 以上
実施例 6	窒化珪素	ムライト	ムライト／ジルコニア	ジルコニア	50回以上	150Hr 以上
実施例 7	複合材	ジルコン	ジルコン／ジルコニア	ジルコニア	50回以上	150Hr 以上
実施例 8	複合材	ムライト	ムライト／アルミナ	アルミナ	50回以上	150Hr 以上
実施例 9	複合材	ムライト	ムライト／イットリア	イットリア	50回以上	150Hr 以上
実施例１０	複合材	ムライト	ムライト／ジルコニア	ジルコニア	50回以上	150Hr 以上
比較例 1	窒化珪素	－	－	アルミナ	10回	10Hr
比較例 2	窒化珪素	－	－	ジルコニア	10回	20Hr
比較例 3	複合材	－	－	アルミナ	10回	10Hr

The property of each ceramic base material and the ingredient of each oxide is as being shown in Table 2.

[0014]

[Table 2]

材料	熱膨張係数 (×10⁻⁶／℃)	融点 (℃)
ジルコン ($ZrO_2 \cdot SiO_2$)	4.4 (200-900℃)	1675
ムライト ($3Al_2O_3 \cdot 2SiO_2$)	5.5 (20-1500℃)	1840
イットリア (Y_2O_3)	9.7 (20-1500℃)	2410-2415
アルミナ (Al_2O_3)	10 (20-1500℃)	2050
ジルコニア (Y_2O_3安定化ZrO_2)	10.6-10.9 (40-1000℃)	2285-2715
窒化珪素	3.5 (40-1200℃)	－
複合材	3.7 (40-1200℃)	－

As shown in said table 1, zircon or a mullite was used for the substrate layer, and yttria, the alumina, or the zirconia was used for the surface layer. The interlayer changed the rate of the ingredient of said substrate layer, and the ingredient of a surface layer, and made it incline. When explained in full detail taking the case of the example 1, the middle class changed [layer / substrate / surface layer / zircon and] the mixed rate of zircon and a zirconia by the zirconia. In this case, the laminating of

the interlayer was carried out to 11 layers of following (1) - (11). An interlayer's mixed rate is a weight ratio.
[0015]
(1) zircon / zirconia = -- 100:0 (2) zircon / zirconia = -- 100:0 (3) zircon / zirconia = -- 85:15 (4) zircon / zirconia = -- 70:30 (5) zircon / zirconia = -- 50:50 (6) zircon / zirconia = 30:70 (7) Zircon/zirconia = 15:85 (9) Zircon/zirconia = 0:100 (10) Zircon/zirconia = 0:100 (11) Zircon/zirconia = also about the 0:100 aforementioned examples 2-10 The substrate layer and surface layer which are similarly shown in Table 1 were taken, and an interlayer's mixed rate was changed.
[0016] The spray condition when forming said substrate layer, and an interlayer and a surface layer was as follows.

溶射機	:	プラズマ溶射装置
アークガス	:	Ａｒ－H_2 またはＡｒ－N_2
電流	:	４５０～７００Ａ
電圧	:	４０～７０Ｖ
粉末供給量	:	２～４０ｇ／分
溶射距離	:	１２０mm
溶射層厚	:	下地層　５０μm以下
	:	中間層　５０μm以下
	:	表面層　５０μm以下

(2) Example of a comparison In formation of an enveloping layer, the examples 1-3 of 1 - 3 comparison formed the direct surface layer in the front face of a ceramic base material, as shown in said table 1. That is, a substrate layer and an interlayer were not formed. The spray condition of a surface layer was the same as said examples 1-10.
[0017] After carrying out heating maintenance of the ingredient of the thermal cycling test aforementioned examples 1-10 and said examples 1-3 of a comparison for 30 minutes in 1400-degree-C long duration annealing and a 1400-degree C electric furnace, into atmospheric air, it took out, the thermal cycling test which carries out air cooling was repeated and carried out, and the number of repeats until exfoliation of a surface coating layer is seen about each ingredient was investigated.
[0018] The result is shown in Table 1. Said examples 1-10 did not cause abnormalities, such as exfoliation and a crack, although 1400 degree-C-150hr annealing and a heat cycle with a room temperature of -1400 degrees C were carried out 50 times. Said examples 1-3 of a comparison exfoliated in ten cycles.
[0019]
[Effect of the Invention] As explained above, according to the ceramic-coating member of this invention, it is effective in the peeling resistance of a base material and an enveloping layer being good, and being excellent in thermal resistance, thermal shock resistance, and corrosion resistance. Moreover, according to the manufacture approach of the ceramic-coating member of this invention, it is effective in the ceramic-coating member which whose peeling resistance of an enveloping layer was good and was excellent in thermal resistance, thermal shock resistance, and corrosion resistance being obtained by the simple approach.

TECHNICAL FIELD

[Industrial Application] This invention relates to the ceramic-coating member excellent in thermal resistance, thermal shock resistance, and corrosion resistance.

PRIOR ART

[Description of the Prior Art] Conventionally, as an elevated-temperature structural material used by the severe condition at an elevated temperature, ceramic ingredients, such as silicon nitride and silicon carbide, are known. The silicon nitride sintering member with the zirconia enveloping layer shown in JP,62-72582,A as a heat-resistant good ceramic ingredient is known.

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to the ceramic-coating member of this invention, it is effective in the peeling resistance of a base material and an enveloping layer being good, and being excellent in thermal resistance, thermal shock resistance, and corrosion resistance. Moreover, according to the manufacture approach of the ceramic-coating member of this invention, it is effective in the ceramic-coating member which whose peeling resistance of an enveloping layer was good and was excellent in thermal resistance, thermal shock resistance, and corrosion resistance being obtained by the simple approach.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, also although such silicon nitride or silicon carbide is called elevated-temperature heat-resisting material, if it is exposed to the combustion gas in which these ingredients have the high-speed rate of flow, high temperature oxidation, high temperature corrosion, etc. will thin down a member in many cases. For this reason, in order to improve endurance about the member exposed to combustion gas with the high-speed rate of flow, it is an important technical problem to raise oxidation resistance.

[0004] Only by carrying out surface coating of the oxide ceramics on the surface of a base material according to the surface coating approach of such conventional oxide ceramics, although the approach of carrying out surface coating of the oxide ceramics for this technical-problem solution is proposed, if long duration use is carried out at an elevated temperature, it will originate in the difference between the coefficient of thermal expansion of a base material, and the coefficient of thermal expansion of oxide ceramics, stress distortion will become excessive by the boundary layer, and an enveloping layer will tend to exfoliate from a base material.

[0005] The purpose of this invention has the good peeling resistance of a base material and an enveloping layer, and it is to offer the ceramic-coating member excellent in thermal resistance, thermal shock resistance, and corrosion resistance, and its manufacture approach.

MEANS

[Means for Solving the Problem] The ceramic-coating member by this invention for attaining said purpose The substrate layer of the oxide which has the coefficient of thermal expansion, the EQC, or the near coefficient of thermal expansion of a base material on the front face of a silicon nitride radical ceramic base material, It is characterized by having the interlayer of the oxide formed in the front face of this substrate layer, and the surface layer of the oxide formed in this interlayer's front face, and having the inclination structure which a coefficient of thermal expansion inclines in order of said substrate layer, an interlayer, and a surface layer, and becomes high gradually.

[0007] Said oxide is two or more sorts chosen from zircon, a zirconia, an alumina, a mullite, and yttria. Said interlayer consists of a mixolimnion of said substrate layer and said surface layer, and he consists of multilayer inclination structure which a coefficient of thermal expansion inclines and becomes high gradually as he makes the mixed rate incline gradually and goes to said surface layer from said substrate layer.

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OPERATION

[Function] Since according to the ceramic-coating member of this invention the device in which the stress distortion between each class etc. is absorbed is generated in order that the value of a coefficient of thermal expansion may consider as the inclination enveloping layer structure which increases gradually as the typical sectional view of an enveloping layer is shown in drawing 1 and it goes to an interlayer 4 and a surface layer 5 from the substrate layer 3 of the enveloping layers 2 formed in the front face of the silicon nitride radical ceramic base material 1, the maximum stress at the time of stress generating is reduced. The ceramic member which has a coating layer with high resistance, such as a thermal shock, by this is obtained.

[0011] According to this ceramic-coating member, thermal shock nature improves by the inclination of the coefficient of thermal expansion of a surface coating layer, the oxidizing quality in an elevated temperature and corrosive are improved sharply, and a reliable ceramic-coating member is obtained.

EXAMPLE

[Example] A substrate layer and the middle class were formed for the front face of a ceramic base material with 3mm [in test piece dimension width of face of 4mm, and thickness], and a die length of 50mm after surface roughening, and the surface layer of an alumina, a zirconia, or yttria was formed in the maximum surface by thermal spraying.

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実施例 9	複合材	ムライト	ムライト／イットリア	イットリア	50回以上	150Hr 以上
実施例１０	複合材	ムライト	ムライト／ジルコニア	ジルコニア	50回以上	150Hr 以上
比較例 1	窒化珪素	－	－	アルミナ	10回	10Hr
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比較例 3	複合材	－	－	アルミナ	10回	10Hr

The property of each ceramic base material and the ingredient of each oxide is as being shown in Table 2.

[0014]

[Table 2]

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ジルコニア（Y_2O_3安定化ZrO_2）	10.6-10.9 （40-1000℃）	2285-2715
窒化珪素	3.5 （40-1200℃）	－
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As shown in said table 1, zircon or a mullite was used for the substrate layer, and yttria, the alumina, or the zirconia was used for the surface layer. The interlayer changed the rate of the ingredient of said substrate layer, and the ingredient of a surface layer, and made it incline. When explained in full detail taking the case of the example 1, the middle class changed [layer / substrate / surface layer / zircon and] the mixed rate of zircon and a zirconia by the zirconia. In this case, the laminating of the interlayer was carried out to 11 layers of following (1) - (11). An interlayer's mixed rate is a weight ratio.

[0015]

(1) zircon / zirconia = -- 100:0 (2) zircon / zirconia = -- 100:0 (3) zircon / zirconia = -- 85:15 (4) zircon / zirconia = -- 70:30 (5) zircon / zirconia = -- 50:50 (6) zircon / zirconia = 30:70 (7) Zircon/zirconia = 15:85 (9) Zircon/zirconia = 0:100 (10) Zircon/zirconia = 0:100 (11) Zircon/zirconia = also about the 0:100 aforementioned examples 2-10 The substrate layer and surface layer which are similarly shown in Table 1 were taken, and an interlayer's mixed rate was changed.

[0016] The spray condition when forming said substrate layer, and an interlayer and a surface layer was as follows.

溶射機	:	プラズマ溶射装置
アークガス	:	Ａｒ－H_2 またはＡｒ－N_2
電流	:	４５０～７００Ａ
電圧	:	４０～７０Ｖ
粉末供給量	:	２～４０ｇ／分
溶射距離	:	１２０mm
溶射層厚	:	下地層　５０μm以下
	:	中間層　５０μm以下
	:	表面層　５０μm以下

(2) Example of a comparison In formation of an enveloping layer, the examples 1-3 of 1 - 3 comparison formed the direct surface layer in the front face of a ceramic base material, as shown in said table 1. That is, a substrate layer and an interlayer were not formed. The spray condition of a surface layer was the same as said examples 1-10.

[0017] After carrying out heating maintenance of the ingredient of the thermal cycling test aforementioned examples 1-10 and said examples 1-3 of a comparison for 30 minutes in 1400-degree-C long duration annealing and a 1400-degree C electric furnace, into atmospheric air, it took out, the thermal cycling test which carries out air cooling was repeated and carried out, and the number of repeats until exfoliation of a surface coating layer is seen about each ingredient was investigated.

[0018] The result is shown in Table 1. Said examples 1-10 did not cause abnormalities, such as exfoliation and a crack, although 1400 degree-C-150hr annealing and a heat cycle with a room temperature of -1400 degrees C were carried out 50 times. Said examples 1-3 of a comparison exfoliated in ten cycles.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the typical sectional view showing the structure of the enveloping layer of this invention.

[Description of Notations]
1 Ceramic Base Material
2 Enveloping Layer
3 Substrate Layer
4 Interlayer
5 Surface Layer